

# Sensors for Water Safety and Security

A. Vaseashta<sup>a</sup>, E. Braman<sup>b</sup>, P. Susmann<sup>b</sup>, Yu. Dekhtyar<sup>c</sup>, K. Perovicha<sup>c</sup>

<sup>a</sup>*Institute for Advanced Sciences Convergence & International Clean Water Institute  
NUARI, 13873 Park Center Rd. Suite 500, Herndon, VA, USA, 20171, e-mail: [prof.vaseashta@ieee.org](mailto:prof.vaseashta@ieee.org)*

<sup>b</sup>*NUARI, 57 Old Freight Yard, PO Box 30, Northfield, VT, USA 05663*

<sup>c</sup>*Biomedical Engineering and Nanotechnologies Institute,  
Riga Technical University, Riga, Latvia*

Identification and prioritization of contaminants arising from occasional release or intentional discharge in unsecured water supplies are of paramount importance to assess national and international capacities to be able to respond, sense/detect, isolate, and mitigate safety and security risk vectors in a timely manner. Using advanced and nanoscale materials, a series of novel point and stand-off sensors/detectors for continuous and in-situ monitoring of inorganic, organic, and microbiological pollutants are described. The study is concurrent to our existing efforts to develop remediation strategies for region specific contaminants, defining water quality, modeling of process function water system design, and enhancing water resiliency. New sensing approaches based on interaction of a semiconductor surface with emitting electrons and metal-complexes-based chiroptical switches are also described.

УДК 33:913:626

## INTRODUCTION

Water is fundamental to sustaining life. Safe, secure, and functional water supplies are indispensable to sustaining modern urban living. A growth in human population and associated increased demands on water supply poses a significant challenge in maintaining adequate yet acceptable water quality in various sectors. Furthermore, adversaries and non-state actors have demonstrated a strong will and interest to wage unconventional war against Western targets despite their limited technological capabilities and lack of sophistication in conducting such operations. In fact, the unsophisticated nature of such threats poses the most significant technical challenge in both point and stand-off detection. It is thus extremely important to monitor, control, and mitigate contaminants using state-of-the-art materials and technologies to maintain “water quality” – typically defined as physical, chemical, and biological characteristics of water in conformity with a set of standards. Water quality is a rather complex subject and is intrinsically tied to the regional ecology, application, and point-of-use, hence standards vary accordingly.

The objective of the present investigation is to study a series of sensors/detectors using nanomaterials and recent state-of-the-art technologies for inorganic, organic, microbiological, pharmaceutical materials, volatile organic compounds (VOCs), Toxic Industrial Chemicals/Toxic Industrial Materials (TIC/TIM), and other intentional or unintentional materials discharged in water by either sampling (point contact) or contact-less (stand-off) methodologies. In particular, we present two new methodologies based on electron emission and metal-based chiroptical switches. Detection methodologies based on nanomaterials and other advanced strategies are capable of ppb/ppt and attomolecule resolution with high selectivity and specificity. For mixed compositions, such methodologies are particularly critical in identifying constituent ingredients. Furthermore, remediation strategies designed based on contamination composition will be more effective to maintain water quality. We also present a water quality management system based on region-specific contaminants. To support urban life style and even mission readiness in battle-space, it is critical to maintain a resilient water supply. Advanced detection schemes and suitable remediation strategies will sustain contamination resilient clean water delivery systems.

## MATERIALS IN REDUCED DIMENSIONS

One- and multi-dimensional nanoscale materials begin to display quantifiable novel characteristics. The onset of deviation from bulk to reduced dimensions has resulted in many unique electrical, optical, and mechanical characteristics [1–3]. For solids, typically reduced dimensions amount to reduction of the coordination number; hence the electrons have less opportunity to hop from site to site, thus reducing kinetic energy of electrons. A higher Coulomb interaction at a site enhances electron correlation and the Mott transition. Furthermore, the symmetries of the system are lowered and the appearance of new boundary

conditions leads to surface and interface states. A change of the quantization conditions alters the eigenvalue spectrum and transport properties of the solid. A high surface area/volume ratio in nanoscale materials alters mechanical and other physical properties and hence surface stresses existing in nanomaterials have a different bonding configuration as compared to bulk atoms. The difference between surface and bulk properties becomes greater as the surface area/volume ratio increases with decreasing structural dimension resulting in better sensing/detection capability. Studies to calculate surface elastic constants using MD simulations, curvature effect using the Cauchy-Born rule, and electronic effects via effective nuclei-nuclei interactions using DFT calculations provide better understanding of surface and interface effects in nanoscale dimensions. Size and surface collectively control interactions of nanoscale materials due to existence of large boundaries in its surroundings and thus interplay of physicochemical interactions. The surface free energy is size dependent and hence increases almost inversely with the decrease of the feature size. Collective response of a nanomaterials-medium system that is attributable to reduced dimensions, viz. size, physical, and chemical surface structure is vital to developing a scientific model that predicts the response and interaction of such a system.

## CHEM-BIO SENSING MECHANISMS

Nanomaterials, such as carbon nanotubes (CNTs), nanoparticles, nanowires, nanocones, nanohorns, quantum dots (QDs), nanoporous materials, etc. are frequently used for chem-bio sensors/detectors. CNTs, being conducting, can act as electrodes, generate electro-chemiluminescence (ECL) in aqueous solutions, and can be derivatized with a functional group facilitating recognition via immobilization of biomolecules. Oxidation of CNTs leads to high concentrations of carboxylic, carbonyl, and hydroxyl groups on the surface, which can readily be derivatized by a variety of reactions allowing linking of biomolecules such as proteins, enzymes, DNA, or even metal nanoparticles. The covalent modification of CNTs facilitates the creation of well-defined probes which are sensitive to specific intermolecular interactions of many chemical and biological systems. Integration of the transducer and probe enables quick, accurate, reagentless and reversible measurement of target analytes. Covalent modification of single-wall CNTs (SWNTs) offers mapping of functional groups at a molecular resolution. Furthermore, chemical processes to link catalysts, such as transition-metal complexes, to the ends of CNTs are useful in creating or modifying the structures at a molecular scale, creating interconnections for electronic devices. During interaction with the polymer coatings, the electrical properties of NTs are altered, enabling detection of the molecules leading to a very sensitive sensing mechanism. Nanoporous silicon and carbon, with porosities of dimensions comparable to those of biomolecules, are used for biosensor applications [4]. The mesoporous carbon matrix is used for stable immobilization of the biological molecule, and C60 serves as an electron mediator. Both C60 and NTs are good electron mediators when used with a mesoporous carbon matrix or modified metal electrodes. CNT-based transducers, however, show a significant advantage over porous silicon due to the well-defined, defect-free structures, and also because the NTs promote homogenous electron transfer reactions [5].

Based on self-assembled monolayers (SAM), Surface Plasmon Resonance (SPR) is used to detect several pathogens [6]. The SPR detection technique is rapid, real-time, label-free, and involves immobilizing antibodies (ABs) by a coupling matrix on the surface of a thin film of noble metal. A main response is the refractive index of the metal film, to which target molecules are immobilized using specific capture molecules or receptors along the surface, which causes a change in the SPR angle. The rates of change of the SPR signal can be analyzed to yield apparent rate constants for the association and dissociation phases of the reaction. Surface enhanced Raman Spectroscopy (SERS) has also been used for chem-bio detection. One possible mechanism of the enhancement of a SERS signal is due to excitation of localized surface plasmons primarily due to physisorption. Chemical enhancement, on the contrary, rationalizes the effect through formation of charge-transfer complexes. The surface sensitivity and selectivity, irrespective of enhancement mechanism, extend its utility to a wide variety of interfacial systems and chemical enhancement can be conducted under ambient conditions for stand-off detection capability.

Nucleic acids offer a powerful tool for recognition and monitoring of many important compounds. Recent advances in molecular biology aid investigation of the effects of proteins and drugs on gene expression viz. gel mobility shift, molecular binding, bio-mimicking, DNA foot-printing and fluorescence-based assays. Most of these methods, however, are indirect and require various labeling strategies. Electrochemical biosensors provide rapid, simple and low-cost point-of-care detection of specific nucleic acid sequences by electrostatic interactions with the negatively charged nucleic sugar-phosphate structure, binding interactions with the DNA double helix, or intercalation between the stacked base pairs of native DNA. Most electrochemical sensors use different chemistries, and employ interactions between the target, the recognition layer and an electrode. Analysis in direct electrochemical DNA sensors is based on a guanine signal where a base-

pairing interaction recruits a target molecule. Development of sensing strategies to maintain critical dynamics of the target capture to generate a sufficient recognition signal is critical.

Transition-metal based chiroptical switches are capable of reversible transition from one stable state to another [7]. Using simple synthetic organic tools and bio-mimetic chemistry, molecular switches can controllably and reversibly respond to external triggers. Molecular redox switches based on helical metal complexes using natural siderophores [8] can readily be monitored spectroscopically. The mechanism provides stand-off detection via molecular sensors whose conformations are influenced by environmental variations. We also present a new methodology for a stand-off detection method based on electron emission. The methodology, mathematical basis, and experimental details are described in a later section. A collection of these methodologies will provide detection of contaminants in water sources thus facilitating development of remediation strategies for safety, security, and sustainability.

## STAND-OFF DETECTION OF WATER QUALITY

Ideally, a set of methodologies adopted to detect contamination in water should be portable, amenable to both field and laboratory analysis, and able to provide fast, reliable, and real-time detection and differentiation of chemical, biological (e.g., bacteria, virus, pathogens), VOC, TIC/TIM, pharmaceutical, and other contaminants. These features facilitate immediate action by service providers if warranted.

### *Disinfection and Remediation of Contamination Strategies*

A series of conventional to state-of-the-art disinfection, remediation and filtration methodologies are used for producing safe, energy-efficient, and cost-saving water purification and wastewater reclamation facilities. Wastewater disinfection aims to reduce the number of microorganisms in holding tanks. Common methods of disinfection include using ozone, UV light, and sodium hypochlorite. However, the most common and inexpensive disinfection methods involve some form of chlorine (e.g., chlorination, chloramines, chlorine dioxide) being highly effective in killing most bacteria, viruses and protozoa, the process exhibits limited effectiveness against certain pathogens, such as cryptosporidium. The eradication of waterborne diseases is an overwhelming challenge that can be addressed through efficient methods of monitoring and detection. Direct pathogen identification and isolation is difficult, if not impossible. Indirect “indicator-organism” based inferences have been used for decades as indicators of contaminated water. Traditional and standard bacterial detection methods for identifying waterborne pathogens are often not suitable for routine monitoring due to their high cost, inadequate sensitivity, or lengthy processing time (up to 7–8 days to yield an answer). Moreover, all conventional methods require *a priori* knowledge of the pathogen. There is a growing global public health concern about waterborne microbial pathogens that is revealed through a complex interaction of social, economic, and ecological factors. Current indicators for water quality do not take into account newly-discovered microbes. It is interesting to note that only ~1% of microorganisms have actually been characterized. The range of new diseases is broadening, antimicrobial resistance is increasing, and waterborne diseases once eradicated are reappearing. Clearly, improvements in routine monitoring and detection are both expedient and necessary.

The advancement of molecular biology and its application in environmental microbiology are promoting methods for rapid detection of waterborne microbial pathogens. Molecular biology-based alternative methods have reduced detection speed – from several days down to a few hours. Advanced nano-enabled biosensors can interact with cells (bacteria, viruses, and protozoa), but, so far, they have not been widely used for detecting waterborne pathogens. Still there is some research that involves using plant roots to sequester Arsenic ions [9]. Then, iron getters employed in holding tanks can reduce iron in water pipes that will in turn inhibit bacterial growth [10]. These innovative approaches as well as those aimed at modelling fluid flow and movement of chemicals in rock formations near aquifers may lead to better detection of salinity and management of freshwater resources.

### *Wastewater Remediation and Contaminant Removal Units*

Remediation and contamination removal systems span the range from reverse osmosis and nanofiltration, electro-deionization, ultra/micro filtration membrane technology, ion exchange resins (ion exchange is a well-proven technology for the removal of a wide variety of trace metal contaminants, including chromium, cadmium, nickel, copper, lead and zinc) to chelating resins and adsorption media. However, membrane filtration, semi-permeable thin barrier sheets used in water treatment processing for less than 50 years, is the leading technology for the specific removal of pollutants and wastewater treatment to high purity standards. Membranes are considered an ideal tool for recycling water due to their extensive abatement range. Advanced

wastewater treatment processes often incorporate a high-pressure reverse osmosis system, among the most effective technologies for removing PFCs, trace pharmaceuticals, and disease-causing bacteria and viruses from water, with lower pressure membrane filtration pretreatment (table 1). The integrated membrane system can remove salts, volatile organic and inorganic chemicals, nitrates, radionuclides, and reduce pathogen exposure, thus offering a customized solution to meet localized clean water needs.

**Table 1.** Wastewater remediation and contaminant removal methods

<b>Filtration Method</b>	<b>Operating Pressure (bar)</b>	<b>Contaminant Removal</b>	<b>Water Treatment Application</b>
Conventional Sand Filtration	0.1–2.0	Large Suspended Matter	Clarification
Membrane Microfiltration	0.2–2.0	Colloids Bacteria	Clarification
Membrane Ultrafiltration	1.0–5.0	Large Organic Molecules, Viruses	Clarification
Membrane Nanofiltration	5.0–20.0	Small Organic Molecules, Divalent Ions	Color, Natural Organic Matter, Micro-pollutant Removal
Membrane Reverse Osmosis	20.0–80.0	All Dissolved Species	Desalination

### WATER QUALITY MANAGEMENT METHODOLOGY

Water purification is complicated due to geography and complex issues requiring individual, local, regional, national, and even international solution platforms. Despite advances in conventional purification and disinfectant systems for both ground and surface water sources employing chlorine dioxide, ozone, and ultraviolet irradiation, there are disease outbreaks from waterborne infections. In addition to microbial contamination from bacteria, protozoans, and viruses, the water supply contains previously undiscovered pathogens and pharmaceuticals such as antibiotics, steroids, and common over-the-counter (OTC) painkillers that affect the younger population more acutely. These types of contaminants call for point-of-use (POU) and point-of-entry (POE) decontaminants.

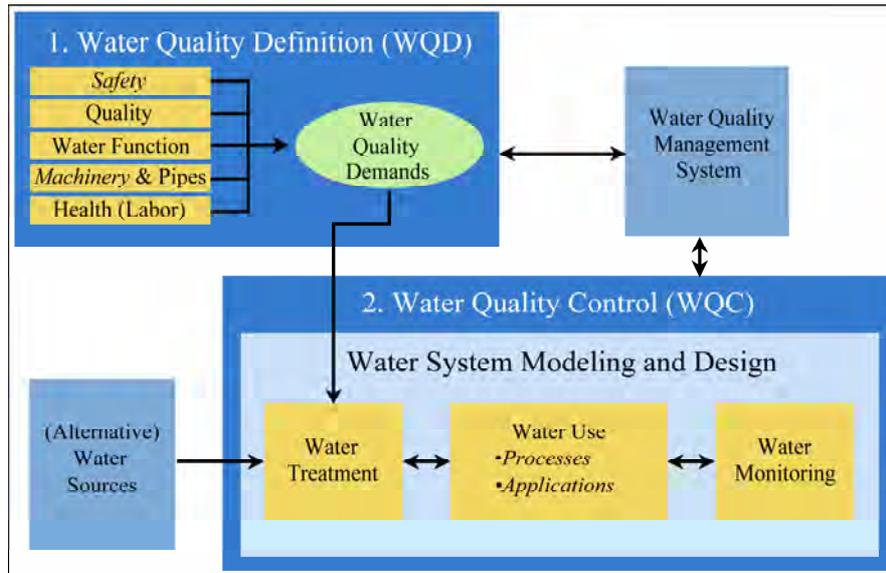
The opportunity nexus for water purification consists of the following components:

- i) Environment – decontamination technologies to minimize environmental impact, globalization, urbanization, and other emerging issues to ensure adequate clean supply of potable water.
- ii) Energy generation – as the energy demand continues to increase, water consumption for such plants is expected to increase between 30–50% (depending upon efforts to reduce consumption of fossil fuels).
- iii) Agriculture – increase in population will require greater water supplies for irrigation and livestock and new mechanisms for enhanced agricultural water conservation and increased recovery, and reuse of irrigation runoffs.
- iv) Health – strains on water supply have a direct effect on access to clean potable water and human health. Toxic levels of arsenic in water supplies are increasing in some parts of the world. Pathophysiology of arsenic includes disruption of ATP production; inhibits pyruvate dehydrogenase and energy-linked reduction of  $\text{NAD}^+$ , mitochondrial respiration, increased hydrogen peroxide production leading to oxidative stress, and metabolic interferences leading to death from multi-system organ failure. Several studies link long-term exposure to small concentrations of As with cancer, cardiovascular, pulmonary, immunological, neurological and endocrine effects; thus necessitating research into efficient methods for removing As from drinking water.
- v): Security – Maintaining water supply chain integrity is an issue of national welfare as water supplies are targets for terrorism. Accordingly, the U.S. environmental protection agency (EPA) has initiated a Water-Sentinel program for the design, development, and deployment of a robust, integrated water surveillance system to provide wide real-time system water quality monitoring, critical contaminants sampling and analysis, and public health surveillance. The Water-Sentinel program uses nanomaterials-based sensors, improvised signal distribution and transmission, and decision support technology.
- vi): Economy – According to the U.S. congressional budget office estimated the late 1990s, the average cost of water and wastewater services makes up ~0.5% of the household income, and that by 2020, the projected costs would be ~0.6–0.9% of the national household income. This is why assurance of abundant clean water is imperative for sustaining economic viability.

#### *Water Quality Definition*

Water quality is typically defined as the physical, chemical and biological characteristics of water in conformity with a set of standards. Because water quality is affected by geography, application, and point-of-

use, so standards vary accordingly. However, based on the proposed methodology, in the present paper, a unified definition of water quality and a set of standards are articulated.



**Fig. 1.** Water quality definition model.

Fig. 1 shows a water quality definition model based on application and point of use. Note that regional differences factor into water treatment methods. Water processing and distribution is described in the following sections.

#### *Management System*

A conceptual schematic view of the proposed water management system is presented in table 2, fig. 2, and fig. 3. The methodology consists of thorough detection of chemical and biological contaminants in water derived from a specific source and of comparing them with an inventory of acceptable maximum contaminants in acceptable quantities according to local or EPA regulations.

**Table 2.** Inventory of maximum allowable contaminants for process water function as per regulatory guidelines

<b>Database Process Water Function (PWF)</b>		
<b>Region 1</b>		
<b>Sector</b>	<b>PWF</b>	<b>Compound &amp; Corresponding Range</b>
Residential	Drinking	Compound 1 [...]; 2 [...]; n [...]
	Cooking	Compound 1 [...]; 2 [...]; n [...]
	Bathing	Compound 1 [...]; 2 [...]; n [...]
	Gardening	Compound 1 [...]; 2 [...]; n [...]
Commercial	Food Service	Compound 1 [...]; 2 [...]; n [...]
	Hospitals & Clinics	Compound 1 [...]; 2 [...]; n [...]
	Aquatics	Compound 1 [...]; 2 [...]; n [...]
	Hotels & Resorts	Compound 1 [...]; 2 [...]; n [...]
Industrial	Semiconductor	Compound 1 [...]; 2 [...]; n [...]
	Power Generation	Compound 1 [...]; 2 [...]; n [...]
	Agriculture	Compound 1 [...]; 2 [...]; n [...]
	Pharmaceutical	Compound 1 [...]; 2 [...]; n [...]

The water derived from aquifers, rivers, water shed, and other available sources will have different contaminants. In designing water purification strategies specific to an application, the limits of contaminants will be different for different applications. Water for drinking and cooking purposes will be subject to standards different from those for water for gardening, for example. Likewise, for industrial applications, water for medical, pharmaceutical and semiconductor processing applications has different levels of acceptable contaminants against water for power generation, aquatics and leisure time.

Based on regional ecology and associated water contaminants, an efficient water purification scheme and a process flowchart are provided in fig. 2; and an overview of the methodology is shown in fig. 3. It is anticipated that such a scheme is likely to produce economical, more efficient, and widely spread purification scheme at the point of use.

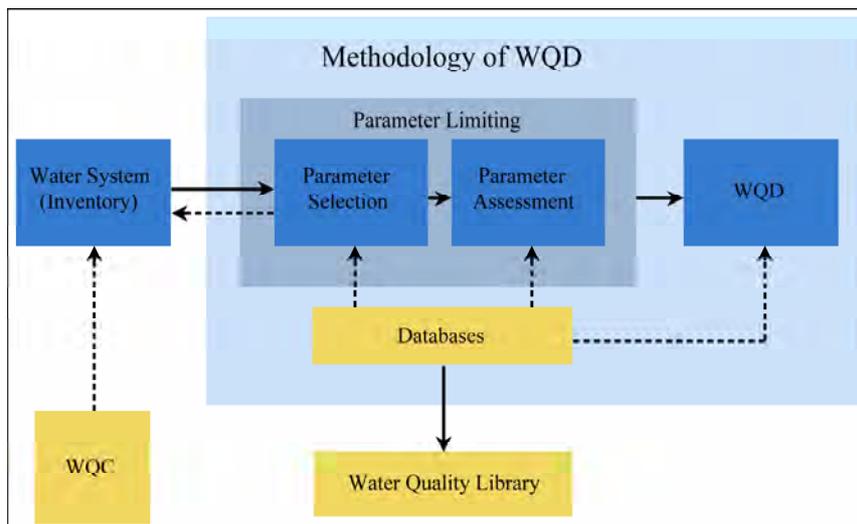


Fig. 2. Water purification decision flow chart.

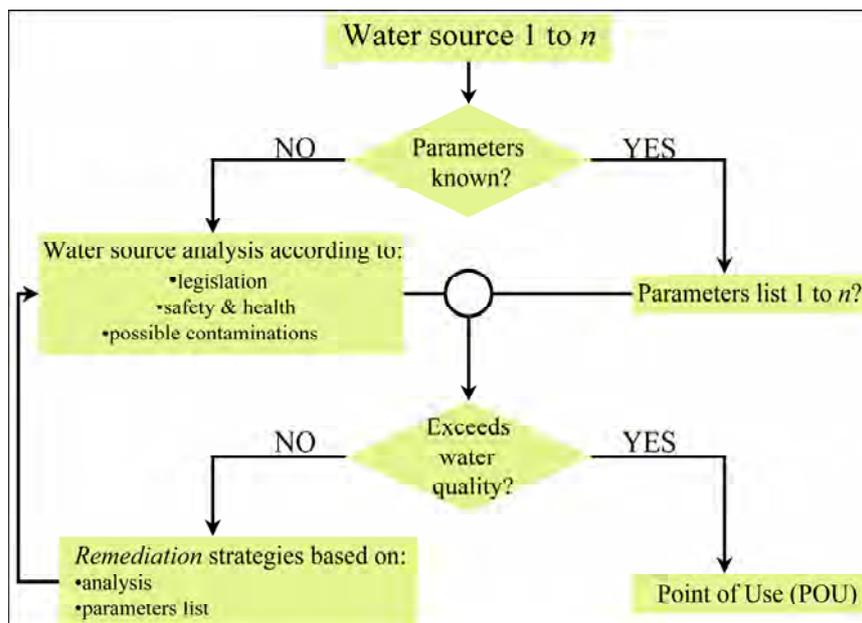


Fig. 3. Region-specific contamination detection and remediation methodology.

It is intended that a similar approach is to be utilized for water purification system for hand-held portable units (similar to Life-Straw, Life-Saver, and other portable water filtration systems); however, with a striking difference that the unit is designed for contaminants specific to a region and is rendered more efficient. The approach is more effective as not all sources of water may contain all contaminants, and hence by selecting remediation strategy, the unit will be more cost effective.

#### ELECTRON EMISISON BASED STAND-OFF DETECTION TECHNIQUE FOR EVALUATION OF CONTAMINANTS

Several methodologies described above, such as SERS, SPR, etc. are remote, contactless, and stand-off detection methodologies. Advance Planning Briefings for Industry (APBI) is a way to keep the industrial base well-informed of the direction of the Chemical and Biological Defense (CBD) program and future requirements of DoD and other agencies such as Department of Homeland Security (DHS) and Transportation Security Agency (TSA). The APBI includes details on Joint Service mid- and long-range science and technology research, development, test, and evaluation plans and programs, future production projections and

emerging military and civilian requirements. One of the requirements is to be able to detect contaminants in water by simply irradiation of electromagnetic (e-m) waves. We present below a mathematical analysis, comparison to experimental methods, and sensitivity estimates using this method.

Typically, contaminants such as microorganisms, biomolecules, VOCs, TIC/TIMs etc. are associated with electrical charge. Proximity or contact of such contaminants to a probing semiconductor surface will alter its electrical potential. The latter contributes to the photoelectron emission electron work function\* ( $\phi$ ) and eventually emission current density ( $I$ ) of electrons escaping the semiconductor due to photoelectron emission (PE) process. Therefore,  $I$  is influenced by the substances of the matter attached to the semiconductor surface and is expressed as:

$$I = A(h\nu - \phi)^m \quad (1)$$

where  $A$  is coefficient of proportionality,  $h\nu$  – energy of the photon that excites the electron,  $m$  – index, and

$$\phi = \phi_0 + \Delta\phi,$$

$\phi_0$  – the value of  $\phi$ , when contaminants are not attached (or in close proximity) to the surface, and  $\Delta\phi$  is increment in  $\phi$  due to the contaminants either attached or in close proximity to the surface.

When the square of the electron emitting area is small in contrast to the surface of the probe (achieved by the local radiation by photons), an increment of  $\Delta\phi$  in accordance with the Gauss law is:

$$\Delta\phi = \frac{\Delta\sigma l}{2\varepsilon_0\varepsilon}$$

$\sigma$  – a surface charge density increment because of the attached molecules;  $\varepsilon_0$  – electric permittivity of vacuum ( $\varepsilon_0 = 8.85 \times 10^{-12}$  F/m),  $\varepsilon$  – electrical permittivity of the matter that electron escapes from, and  $l$  – electron mean free path,

$$\Delta\sigma = \rho N_s$$

$\rho$  – coefficient of proportionality (the charge contributing by each attached ion/molecule/particle – IMP),  $N_s$  – surface density of IMP located on the surface contributing to  $\sigma$ .

As a rule, PE is detected under vacuum conditions. Therefore, it is necessary to conduct modeling and testing of a control test sample with PE in a vacuum chamber. In this case

$$dN_s = \beta b N^{2/3} dt$$

$\beta$  – rate of the IMP deposition on the surface,  $b$  – sticking coefficient that characterizes a probability for the IMP to be attached to the surface,  $N$  – concentration of the attaching particles in gas above the surface, and  $t$  – time.

Because  $N_s = 0$ , when  $t = 0$ , so

$$N_s = \beta b \int_0^t N^{2/3} dt.$$

For a limited source of  $N$  and long exposure of the surface,

$$\frac{\partial N}{\partial t} = -aN$$

Where,  $a$  – the rate of change  $N$  (decreasing).

Because  $N = N_0$ , when  $t = 0$

$$N = N_0 \exp(-at)$$

and

$$N_s = \frac{3\beta b N_0^{2/3}}{2a} (1 - \exp(-\frac{2}{3} at)).$$

Taking into account that at  $t \rightarrow \infty$  ( $t = t_\infty$ )

$$b = \frac{N_s}{N_0^{2/3}},$$

---

\* A minimal energy that the electron needs to consume to escape.

we obtain

$$\frac{3\beta b}{2a} = 1$$

and

$$N_s = bN_0^{2/3}[1 - \exp(-\frac{2}{3}at)].$$

Substituting the above in  $I$ ,

$$I(t) = A\{h\nu - [\varphi_0 + \frac{l\rho b}{2\varepsilon_0\varepsilon}N_0^{2/3}(1 - \exp(-\frac{2}{3}at))]\}^m. \quad (2)$$

From (1) and (2), we find that the highest response of  $I$  (amplification of  $I$ ) using a variation of  $\varphi$  is achievable, if

(i):

$$m > 1, \\ h\nu - \varphi > 1,$$

$$h\nu - [\varphi_0 + \frac{l\rho b}{2\varepsilon_0\varepsilon}N_0^{2/3}(1 - \exp(-\frac{2}{3}at))] > 1,$$

(ii):

$$m < 1, 1 > h\nu - \varphi > 0,$$

$$1 > h\nu - [\varphi_0 + \frac{l\rho b}{2\varepsilon_0\varepsilon}N_0^{2/3}(1 - \exp(-\frac{2}{3}at))] > 0.$$

However the response of  $I$  can be enhanced if PE is detected, if the sample is heated. If  $h\nu - \Phi > 1$ , then formula (1) is transformed [11] using the Richardson-Deshman (RD) formula

$$I(T) = \text{const}T^2 \exp\left(-\frac{\Phi}{kT}\right) \quad (3)$$

$k$  – Boltzmann constant and  $T$  – temperature, and

$$I(T) = A_T T^2 \left[ \frac{\pi^2}{6} + \frac{(h\nu - \Phi)^2}{2kT} - \exp\left(-\frac{h\nu - \Phi}{kT}\right) + \frac{1}{4} \exp\left(-2\frac{h\nu - \Phi}{kT}\right) - \dots \right] \quad (4)$$

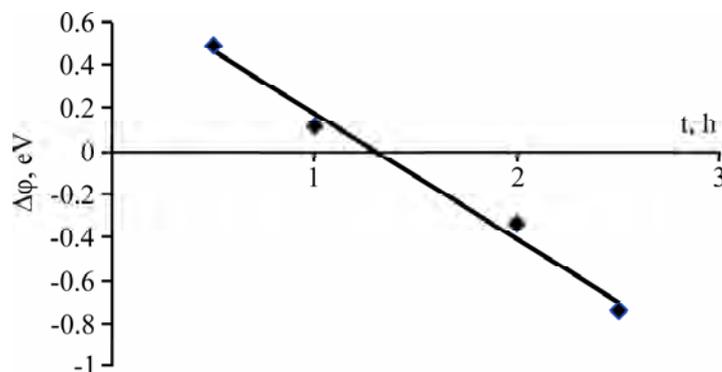
where we demonstrate exponential dependence on  $\varphi$  ( $A_T$  – coefficient of proportionality).

The above approach was verified by a series of experiments. A typical semiconductor Si was selected as an example, which is characterized with a relatively small value of  $\varepsilon = 11.9$  [12], to optimize the influence of  $\Delta\varphi$  on  $I$ . The photoinduced electron transitions in silicon are indirect and the index  $m$  has the highest possible value at  $m = 2.5$  [13] that provides higher gain in  $I$  as a function of  $\Delta\varphi$ , when  $(h\nu - \varphi) > 1$ .

To test the theoretical construct experimentally, benzene molecules were employed. Hydrogen is the most polarized ion of benzene that contributes to the sticking of benzene to Si and therefore, changes in  $\Delta\varphi$ . First, PE was measured from the surfaces of the prepared specimens that were subsequently heated. After the specimens were positioned in a substrate holder, a drop of benzene (volume  $0.08 \text{ cm}^3$ ) was introduced. The benzene was evaporated during ~15 seconds as it was observed. Next, the specimens were heated and PE measured once again. The difference between ( $\Delta Q$ ) – the total emitted charge detected from the coated with benzene specimens and the same uncoated, was the index of  $N_s$  of the attached benzene molecules.

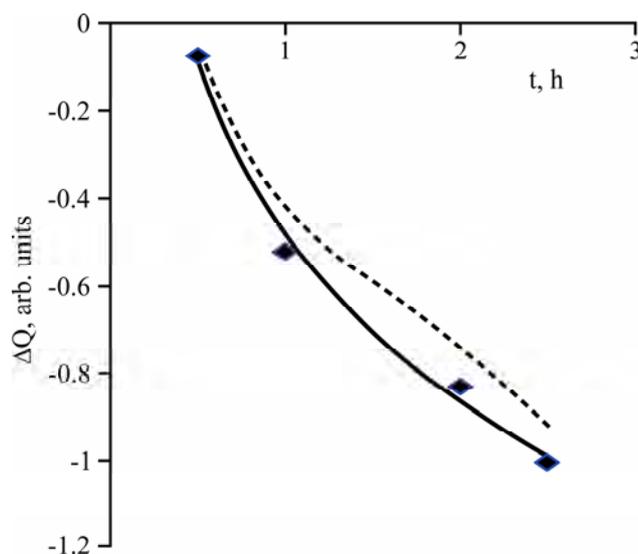
The specimens were prepared from Si on a mirror-like polished surface ( $p$ -type conductivity, partial resistance  $10 \text{ } \Omega\text{-cm}$ , thickness  $0.2 \text{ mm}$ ) diced to sizes  $2 \times 2 \text{ cm}^2$ . Before the experiment the specimens were cleaned using standard wafer cleaning methods. PE was measured in the spectrometer [14], under vacuum conditions of  $10^{-1} \text{ Pa}$ . Heating of the specimens was provided from the room temperature to  $400^\circ\text{C}$ , at the rate of  $0.3^\circ\text{C/sec}$ . To maximally clean the surfaces of the specimens before the benzene exposure they were annealed in the spectrometer several times until the dependence of  $I$  on  $T$  was stabilized. The spectrometer was

equipped with both an ultraviolet Xenon tube generating the unremitting light spectrum and a monochromator to select  $h\nu$ . Since  $\phi_0$  of Si is equal to 4.5 eV [15] and  $m > 1$ , PE was induced by the 5.8 eV photons. The maximal signal of  $I$  was detected in a range at 400–450°C. To verify  $\Delta\phi$  dependence as a function of  $t$ , the benzene-induced increments of  $\phi$  on  $t$  (fig. 4) were calculated as the derivation of  $\ln [(I(T)/T^2)]$  on  $1/kT$  (3) in the same  $T$  range. The graphs  $\ln [(I(T)/T^2)]$  on  $1/kT$  was plotted as the straight lines. Fig. 4 gives evidence supporting the above model.



**Fig. 4.** Dependence of  $\Delta\phi$  on  $t$ .

The value of  $\Delta Q$  increases approximately 10 times as a function of  $t$ . The maximal quantity of benzene molecules was around  $8.8 \cdot 10^{-4}$  mol or  $N_0 = 6.7 \cdot 10^{18}$  molecules/cm<sup>3</sup> ( $N_0$  was estimated when the benzene drop was entirely evaporated into the specimen holder; the benzene is characterised by the molecular mass 78.11 g/mol and density 0.8765 g/cm<sup>3</sup> [16]).



**Fig. 5.** Dependence of  $\Delta Q$  on  $t$  (experiment – solid line, calculations – dashed line).

Fig. 5 demonstrates the increment of  $Q$  obtained from the experiment and numerical calculation of (4). One could assume that during the experiment the Si surface was coated with a benzene monolayer (or several monolayers). Because one monolayer consists of  $\sim 10^{15}$  molecules/cm<sup>2</sup> the sensitivity of the PE-based Si sensor is estimated as the ratio of the maximal value of the detected  $\Delta Q$  (55000 electrons/cm<sup>2</sup>) to  $10^{15}$  molecules/cm, i.e.  $10^{-11}$  electron/molecule. Because PE current obeys Poisson statistics [11] and the detected minimal value of  $\Delta Q$  was 4000 electrons/cm<sup>2</sup>, a threshold to detect benzene molecules is around  $4000^{1/2}$  electrons/ $10^{-11}$  electron/molecule =  $6.3 \cdot 10^{10}$  molecules.cm<sup>-2</sup> or  $\sim 10^{-5}$  molecular layer. This corresponds (at the  $10^{-4}$  sticking coefficient [17]) approximately to  $N \sim 10^{21}$  molecules/cm<sup>3</sup> or to the concentration  $\sim 1\%$ . Although the calculations conducted here are generic, the model shows two important points – namely, that a stand-off detection of contaminants in close proximity or in contact with a probe can be performed using electron emission present in very small concentrations, and, also, that the method shows some initial promising results which need further investigations.

## CONCLUSIONS

Recent progress in sensor platforms based on nanostructured materials has significantly contributed to data collection, processing, and recognition so as to enable the direct detection of chem-bio agents in a label-free, parallel, and multiplexed format with high sensitivity and specificity. Using technological advances,

more exactly, nanomaterials and convergence of advanced sciences, identification, prioritizing, and remediation of contaminants specific to regional ecology, is proposed in this investigation. The concept of photoelectron-emission-based Si sensor is offered to test evaporated pollutions. The threshold to detect benzene molecules is expected around ~ 1% or less and can be applied to other molecules. In addition, a new sensing methodology using transition-metal-based chioptical switches is suggested. It is extremely important to monitor, control, and maintain water quality – typically defined as physical, chemical and biological characteristics of water in conformity with a set of standards. To maintain water quality in an efficient manner, a methodology is proposed which is based on remediation of regional contaminants specific to the point of use. Such an approach is likely to be economical viable. It is to be further noted that not all countries have adopted a uniform set of guidelines for water quality. The proposed methodology is assumed to bring uniformity in standards of water purification across the globe.

## REFERENCES

1. Vaseashta A., Dimova-Malinovska D., Marshall J. *Nanostructured and Advanced Materials*, Springer Science and Business Media: Dordrecht, 2005.
2. Vaseashta A., Mihailescu I. *Functionalized Nanoscale Materials, Devices, and Systems*, Springer Science and Business Media: Dordrecht, 2008.
3. Magarshak Y., Kozyrev S., Vaseashta A. *Silicon Versus Carbon: Fundamental Nanoprocesses, Nanobiotechnology and Risks Assessment*, Springer Science and Business Media: Dordrecht, 2009.
4. Lin V.S.Y., Motesharei K., Dancil K.S., Sailor M.J., Ghadiri M.R. A Porous Silicon-based Optical Interferometric Biosensor. *Science*. 1997, **278**, 840–843.
5. Wang, J. CNT Based Electrochemical Biosensors: A review. *Electroanalysis*. 2005, **17**, 7–14.
6. Vaseashta A., Irudayaraj J.J. Nanostructured and Nanoscale Devices and Sensors. *Optoelectronics and Advanced Materials*. 2005, **7**, 35–42.
7. Zelikovich L., Libman J., Shanzer A. Molecular Redox Switches Based on Chemical Triggering of Iron Translocation in Triple-stranded Helical Complexes. *Nature*. 2002, **374**, 790–792.
8. Kikkery R., Traboulsi H., Raboulsi H., Humbert N., Gumienna-Kontecka E., Arad-Yellin R., Melman G., Elhabiri M., Albrecht-Gary A., Shanzer A. Toward Iron Sensors: Bioinspired Tripods Based on Fluorescent Phenol-oxazoline Coordination Sites. *Inorg. Chem*. 2007, **46**, 2485–2497.
9. Tripathi R.D. et al. Arsenic Hazards: Strategies for Tolerance and Remediation by Plants. *Trends in Biotechnology*, 2007, **25**, 158–165.
10. Vaseashta A. *Security of Industrial Water Supply and Management*, Technological Advances in Industrial Water Safety and Security, NATO Science for Peace and Security Series C: Environmental Security, Springer Science and Business Media: Dordrecht 2011, p. 55–67.
11. Dobrecov L.N., Gomoyunova M.V. *Emission Electronics*. Moscow Nauka, 1966, p. 564 (In Russian).
12. Kane E.O. Theory of Photoelectric Emission from Semiconductors. *Phys. Rev*. 1962, **127**, 131–141.
13. Akmene R.J., Balodis A.J., Dekhtyar YU.D., Markelova G.N, Matvejevs J.V., Rozenfelds L.B., Sagalovch G.L., Smirnovs J.S., Tolkchov A.A., Uminsh A.I. Exoelectron Emission Spectrometre Complete Set of Surface Local Investigation, *Поверхность: физика, химия, механика*. 1993, **8**, 125–128.
14. <http://environmentalchemistry.com/yogi/periodic/Si.html>, Nov., 2010.
15. Sagalovich G.L., Dekhtyar Yu.D. Photothermostimulated Exoelectron Emission from Crystalline Silicon Containing Edge Dislocations and Point Defects. *Physica Status Solidi(A)*. 1987, **102**, 665–677.
16. Thanailakis A., Ioannou D.E., Reed C.M. Hydrogen Adsorption on silicon (111) Surfaces Studied by Auger Electron Spectroscopy. *Solid State Communications*. 1982, **44**, 669–671.
17. Biedermann A., Knoesel E., Hu Z., Heinz T.F. Dissociative Adsorption of H<sub>2</sub> on Si(100) Induced by Atomic h. *Phys. Rev. Lett*. 1999, **83**, 1810–1813.

Received 01.02.12

## Реферат

Идентификация и ранжирование загрязняющих веществ, появляющихся в результате случайных или преднамеренных выбросов в неохранные источники водоснабжения, имеют первостепенное значение для оценки возможностей своевременного обнаружения, изолирования и смягчения угроз национальной и международной безопасности. Рассмотрено использование передовых и наноразмерных материалов, новых точечных, выносных датчиков/детекторов для непрерывного in situ мониторинга неорганических, органических и микробиологических загрязнителей. Исследования отражают усилия по разработке стратегий для восстановления регионов (характеризуемых специфическими загрязняющими веществами) с учетом показателей качества воды, а также моделирования функций системы водоснабжения и повышения надежности воды. В работе рассмотрены новые подходы к сенсорам загрязнений, основанные на взаимодействии поверхности полупроводника с загрязнением и последующей эмиссией электронов, при применении металлокомплексных переключателей.